

ELASTIC PROPERTIES OF HMX

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Abstract. Atomistic molecular dynamics simulations have been used to calculate isothermal elastic properties for β -, α -, and δ -HMX. The complete elastic tensor for each polymorph was determined at room temperature and pressure via analysis of microscopic strain fluctuations using formalism due to Rahman and Parrinello [*J. Chem. Phys.* **76**, 2662 (1982)]. Additionally, the isothermal compression curve was computed for β -HMX for $0 \leq p \leq 10.6$ GPa; the bulk modulus K and its pressure derivative K' were obtained from two fitting forms employed previously in experimental studies of the β -HMX equation of state. Overall, the results indicate good agreement between the bulk modulus predicted from the measured and calculated compression curves. The bulk modulus determined directly from the elastic tensor of β -HMX is in significant disagreement with the compression curve-based results. The explanation for this discrepancy is an area of current research.

INTRODUCTION

This work is part of an ongoing effort to predict the thermophysical and elastic mechanical properties of high-explosive (HE) crystals and liquids using atomistic simulation techniques. In the case of HMX, we have reported calculations of the structural properties of the three pure crystal polymorphs,^{1,2} and the shear viscosity³ and thermal conductivity⁴ of the liquid phase. These kinds of information are required as input to “mesomechanics models” in which the explosive crystallites and polymeric binder in a plastic-bonded explosive (PBX) are resolved within a hydrodynamic simulation framework.⁵

In the present report we summarize calculations of the elastic properties of β -, α -, and δ -HMX. In particular, we apply formalism due to Rahman and Parrinello⁶ in which the elastic tensor is expressed in terms of fluctuations of the microscopic strain tensor obtained from an isothermal-isobaric (NpT) simulation. For the case of β -HMX, we compare

the calculated and measured isothermal compression curves ($T=295$ K, $0 \leq p \leq 10.6$ GPa) and the initial bulk modulus K and pressure derivative $K'=dK/dp$ to experimental values. Finally, we compare the bulk modulus determined in this way to the one predicted directly from the elastic tensor.

COMPUTATIONAL DETAILS

Our studies were performed in the isothermal-isobaric (NpT) statistical ensemble. Periodic boundary conditions corresponding to a general, triclinic primary cell were used. The simulations were performed using the same force field as in our previous studies of HMX.¹⁻⁴ The development⁷ and implementation¹ of the force field are described elsewhere. We note that our simulations include all degrees of freedom other than covalent bond stretching motions, which were constrained to equilibrium values using the SHAKE⁸ algorithm.

Primary simulation cells containing 48 and 96 molecules were used for β -HMX, corresponding to 24 (4x2x3) and 48 (4x4x3) unit cells, respectively. Primary cells containing 64 and 96 molecules were used for α - and δ -HMX, corresponding to 8 (2x1x4) and 16 (4x4x1) unit cells, respectively. Electrostatic interactions were treated using the standard Ewald summation.⁸ Non-bonded interactions were truncated at 10 Å. A fixed time step size of one fs was used in all cases. Equilibration runs of one ns duration were performed, followed by multi-nanosecond production runs during which data were collected for subsequent analysis. All of the calculations were performed at $T=295$ K.

DATA ANALYSIS

Rahman and Parrinello⁶ showed that the fourth-rank elastic tensor for an anisotropic crystalline solid can be calculated directly from fluctuations of the microscopic strain tensor:

$$C_{ijkl} = \frac{kT}{\langle V \rangle} \langle \mathbf{e}_{ij} \mathbf{e}_{kl} \rangle^{-1}, \quad (1)$$

where $\langle V \rangle$ is the average volume at a given temperature T . The instantaneous strain tensor is given by

$$\mathbf{e} = \frac{1}{2} \left[\mathbf{h}^T \left(\mathbf{r} - \mathbf{r}_0 \right) + \left(\mathbf{r} - \mathbf{r}_0 \right)^T \mathbf{h} \right], \quad (2)$$

where \mathbf{h} is the matrix that transforms between Cartesian and scaled coordinates, superscript T denotes matrix transpose, and \mathbf{h}_0 is the reference state of the system at a given p - T state, corresponding to the average volume and shape. Equation (2) is readily constructed from a suitably large set of observations from a molecular dynamics trajectory.

The fourth-rank elastic tensor \mathbf{C} can be expressed in second-rank form through the use of Voigt notation. The particular form for \mathbf{C} is determined by the symmetry class for a given crystal e.g., monoclinic, orthorhombic, and hexagonal for β -, α - and δ -HMX, respectively).

Two experimental studies of the isothermal compression of β -HMX have been reported.^{9,10} In both cases, the compression data were used in conjunction with equation of state fitting forms for $p=p(V;T)$ to extract values for the initial bulk modulus K and its pressure derivative K' . Olinger, Roof, and Cady⁹ used a fitting form

$$p(V) = \frac{V_0 - V}{[V_0 - s(V_0 - V)]^2} c^2 \quad (3)$$

based on the hugoniot jump conditions in the pseudo- (U_s, U_p) plane, where for a linear relation

$$U_s = c + s U_p; \quad c = \sqrt{K/r}; \quad s = (K' + 1)/4. \quad (4)$$

Yoo and Cynn¹⁰ used the third order Birch-Murnaghan equation of state

$$p(V) = \frac{3}{2} K \left[h^{-7/3} - h^{-5/3} \right] + \frac{3}{4} (K' - 4) (h^{-2/3} - 1) \quad (5)$$

where $h = V/V_0$. We have applied both of these fitting forms to our simulated compression data for β -HMX, for comparison of the resultant values of K and K' to experiment as well as to values of K derived directly from the elastic tensor. (A recent re-analysis of both sets of experiments and fittings forms is presented elsewhere.¹¹)

RESULTS AND DISCUSSION

Elastic Tensors for the Polymorphs

The calculated elastic tensor for β -HMX is depicted in Fig. 1, for primary simulation cells containing $N=48$ and 96 molecules.¹² A partial experimental determination for β -HMX has been reported by Zaug;¹³ those results are also included in Fig. 1.¹⁴ The coefficients C_{11} , C_{33} , C_{55} , C_{15} , and C_{35} were well determined in Zaug's experiment; thus, the comparison between our results and his is most meaningful for those cases. Specific values of the thirteen elastic coefficients for β -HMX, $N=96$, are (GPa): $C_{11}=19.4$, $C_{22}=17.5$, $C_{33}=17.8$, $C_{44}=9.1$, $C_{55}=9.2$, $C_{66}=9.8$, $C_{12}=5.9$, $C_{13}=8.4$, $C_{23}=8.2$, $C_{15}=-1.1$, $C_{25}=3.2$, $C_{35}=0.2$, and $C_{46}=2.4$.

The nine elastic coefficients for α -HMX are: $C_{11}=30.3$, $C_{22}=22.7$, $C_{33}=29.9$, $C_{44}=0.6$, $C_{55}=3.1$, $C_{66}=2.9$, $C_{12}=5.3$,

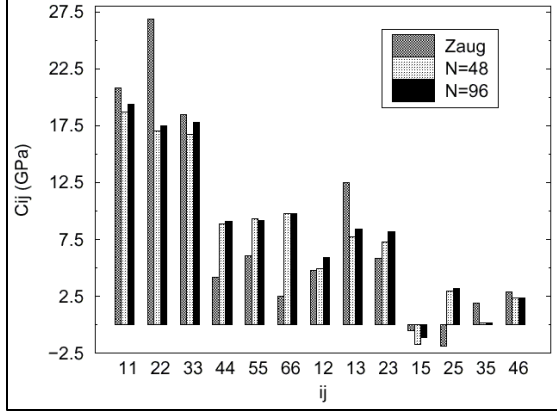


FIGURE 1. Elastic coefficients for β -HMX.

$C_{13}=12.0$, and $C_{23}=5.2$. The five independent elastic coefficients for δ -HMX are: $C_{11}=14.5$, $C_{33}=18.3$, $C_{44}=4.7$, $C_{12}=9.1$, and $C_{13}=10.5$; the four remaining ones are defined by symmetry, namely: $C_{22}=C_{11}$, $C_{55}=C_{44}$, $C_{66}=C_{11}-C_{12}$, and $C_{23}=C_{13}$.

Effective bulk and shear moduli, K and G , can be derived from the elastic tensor. Voigt average values of these parameters are $(K, G)=(11.1, 7.8)$, $(14.2, 5.3)$, and $(11.1, 4.1)$ GPa for β - ($N=96$), α -, and δ -HMX, respectively. It is of interest that, while the predicted values of K for β - and δ - are equal, the value of G for δ is only about half as large as for β .

Isothermal Compression Curve Fits

Simulated and measured compression curves for β -HMX are shown in Fig. 2. The agreement between experiment and simulation is qualitatively good, though not quantitatively correct: at the highest pressure considered here, 10.6 GPa, the percent difference between our compression ratio V/V_0 and that of Yoo and Cynn is 4.6%. (Note that there is also noticeable disagreement between the two experiments.) Overall, the simulation results are in better accord with the data of Olinger *et al.* than with that of Yoo and Cynn.

Equation 4 is trivially linear in c and s . Equation 6 can be expressed as a linear function with axes $x=[h^{-2/3}-1]^{-1}-3$ and $y=2p(V)\{3[h^{-7/3}-h^{-5/3}][h^{-2/3}-1]f^1$, for which the slope and intercept are K and $3KK'/4$, respectively. We fit our compression curve results to both Eq. 5 and 6, for three intervals: $p \leq 1$ GPa, $p \leq 10.6$ GPa, and $1 \text{ GPa} \leq p \leq 10.6$ GPa; we also fit

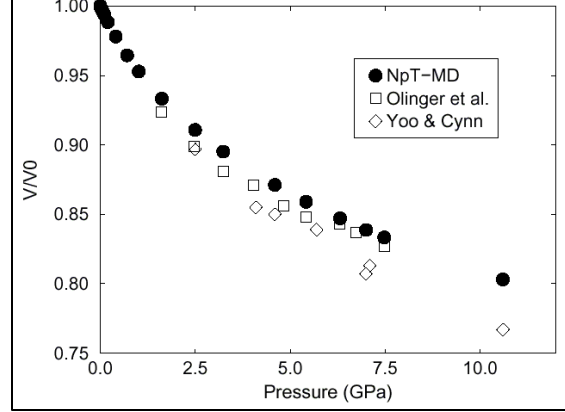


FIGURE 2. Compression curves for β -HMX. Simulation results correspond to $N=96$; “Olinger *et al.*” and “Yoo & Cynn” refer to Refs. 9 and 10, respectively.

the results in the U_s - U_p plane to a quadratic function on each of these intervals. Of the nine fits, seven were quite good ($R^2 \geq 0.998$), one was acceptable ($R^2=0.98$), and one was poor ($R^2=0.24$, corresponding to a quadratic fit of Eq. 5 for $p \leq 1$ GPa; henceforth ignored).

Comparisons Among the Results

The results are collected in Fig. 3, where we also include the conclusions from a recent re-analysis of the experimental data (Ref. 11, Table 1). A number of points are immediately obvious. (1) The values of both K and K' span large ranges: ~ 10 -17 GPa for K and ~ 4 -18 for K' . (2) Values of K and K' extracted from EOS fits to the simulation data are consistent with the experiments. (3) U_s - U_p fits to the experimental data sets yield smaller error bars than do the Birch-Murnaghan ones. (4) Most interestingly, *the value of K predicted from the elastic tensor, 11.1 GPa, is significantly lower than the cluster of values obtained from equation of state fits to the compression results.*

It is important to understand the cause for the discrepancy between the tensor-derived and fitted values of K from the simulation data. There are a number of possible explanations. Finite-size effects may be a factor, although examination of Fig. 1 does not support this conclusion (unless quite large simulations are required to reveal the problem). Simulations for both larger and smaller primary cells are underway.

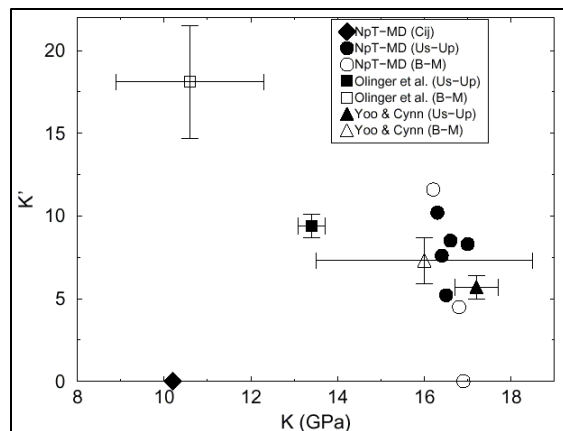


FIGURE 3. Summary of predicted and measured values of K and K' for β -HMX. Us-Up and B-M denote hughoniot and Birch-Murnaghan fitting forms, respectively. Points with $K'=0$ correspond to cases where no values are available [NpT-MD (Cij)] or for which an aphysical value ($K'<0$) was obtained from the fit [NpT-MD (B-M), for the specific case $p \leq 1$ GPa].

Another potential source of difficulty is the necessity to choose a value of the effective “cell mass” that controls the strength of the coupling of the lattice degrees of freedom to the barostat in the NpT-MD algorithm. We have chosen a value of $w=8.0 \times 10^{-4}$ fs⁻¹ for the simulations discussed here. In order to test the effect of large changes in the coupling parameter, we performed a simulation using a trial value $w_t=1.2 \times 10^{-3}$ fs⁻¹ ($w_t/w=3/2$). The first moment $\langle V \rangle$ of the distribution is unaffected by the change, whereas, for the simulation times $t_w=5.0$ ns and $t_{wt}=2.5$ ns considered, the second moment (variance) does differ somewhat. The bulk modulus is given in terms of volume fluctuations by $K=s_V^2[\langle V \rangle kT]^{-1}$, which yields $K_w=11.3$ GPa and $K_{wt}=14.6$ GPa. (Note that the former value agrees well with the prediction for the elastic tensor, providing a cross check of the correctness of that calculation.)

Given this practical sensitivity to a somewhat “arbitrary” parameter, we have undertaken a series of calculations based on a hybrid NpT-MD/Monte Carlo scheme in which volume/shape changes in the system are sampled using Monte Carlo, thereby eliminating the barostat parameter, while canonical ensemble NVT-MD trajectory segments are used to explore phase space for a given system volume and shape.

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- ¹² It is necessary to specify the crystal orientation relative to an orthogonal, lab-fixed frame. For **a**-HMX, *a*, *b*, and *c* are directed along the \hat{x} , \hat{y} , and \hat{z} axes, respectively, in a right-handed cartesian frame (Fdd2 spacegroup). For **b**-HMX, *a* is directed along \hat{x} , *b* is along \hat{y} , and *c* is in the $\hat{x}\hat{z}$ plane ($P_{21/n}$). For **d**-HMX, *a* is directed along \hat{x} , *b* is in the $\hat{x}\hat{y}$ plane, and *c* is along the \hat{z} axis ($P6_1$).
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- ¹⁴ Zaug [Ref. 13] chose a different orientation in his experiments on **b**-HMX; we have transformed the elastic tensor presented in Ref. 13 to coincide with the choice made in the present work.